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ISOTOPIC COMPOSITION OF CARBON MONOXIDE IN ST. LOUIS, MISSOURI AREA

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The concentration and isotopic composition of carbon monoxide were determined in air samples taken in the St.Louis, Missouri area. This information is used to follow the plume for a major city like St. Louis. Urban air could be detected as far as 47 miles downwind of the city. The effect of local emissions in rural areas was found to be minimal. Diurnal studies demonstrated an inverse relationship between carbon monoxide concentration and oxygen and carbon isotopic ratios during the night. A parallel relation was found during the daylight hours.

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ABSTRACT

The concentration and isotopic composition of carbon monoxide were determined for air samples taken in the vicinity of St. Louis, Missouri, to provide information as to the movement of the pollutant plume from the city. Urban air was detected as far as 48 miles downwind of St. Louis; however, movement of the pollutant plume was not detected. The effect of engine carbon monoxide produced along a highway in a rural area was found to be minimal three miles downwind of the highway. Diurnal studies demonstrated an inverse relationship between carbon monoxide concentration and oxygen and carbon isotopic ratios during the night. A parallel relation prevailed during the day.

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SECTION I

INTRODUCTION

Studies by Stevens et al[1] have indicated significant variations in the abundances of oxygen isotopes found in carbon monoxide (CO) from different sources. A conclusion of this past work is that the $\partial(^{18}O/^{16}O)$ ratio of oxygen in CO found in rural areas is as much as 15 parts per thousand (‰) less than that found in urban areas, where combustion processes are the principal source of CO. Thus, it was hoped that the variation in oxygen isotopic composition, as a function of location in an urban area, might provide insight to the movement of air in such an area and serve as a natural tracer. Carbon isotope ratios do not appear to be as potentially useful, but they might in some cases be used to identify sources of CO because of the variation in isotopic composition of carbon in fuels.

Three experiments were conducted in the St. Louis, Missouri, area to sample the pollutant plume as it moved from the city. Samples were taken approximately 30 miles upwind of the city, in the city at 12th and Clark at the Continuous Air Monitoring Project (CAMP) Station and from 18 to 48 miles downwind of the city. In two of the cases, June 27 and November 13-14, 1973, all the downwind samples showed measurable contributions of engine CO. In the other case, July 17, 1973, the downwind samples showed negligible contributions of engine CO.

Due to difficulties in exactly locating the plume, which can have a sinuous pattern[2], a location closer to the city center was chosen and samples were taken at this point over a period of time. The $\partial(^{18}O/^{16}O)$ ratio indicates the contribution of combustion produced CO was ~70%, without any pronounced indication of a peak corresponding to the morning traffic rush.

Additional samples were collected in the St. Louis area in plastic bags for the Chemistry and Physics Laboratory (CPL) of the Environmental Protection Agency. These samples were analyzed by them for acetylene and other hydrocarbons.

Two experiments were conducted to evaluate the changes in concentration and isotopic composition of CO generated by automobile traffic on a major highway in a rural area. Both CO concentration and the $\partial(^{18}O/^{16}O)$

ratio fall off very rapidly, and within three miles the contribution of combustion CO is minimal.

Three experiments were conducted to determine the diurnal changes in concentration and isotopic ratios of CO in a predominantly agricultural area. In these experiments there appears to be a natural sink for the CO with some fractionation also taking place.

SECTION II

CONCLUSIONS

The oxygen isotopic ratio ($^{18}O/^{16}O$) of carbon monoxide is a sensitive indicator for fossil fuel combustion products in the atmosphere. Evidence of urban air was seen as far as 48 miles downwind of the city of St. Louis, Missouri. However, movement of the pollutant plume was not detected. Diurnal studies indicate that there is some carbon monoxide removal process operating during the night, and that production of carbon monoxide from all sources during the day appears to exceed removal processes during the day. The relationship between methane or ethylene and carbon monoxide is proportional for all locations and times and either of these two hydrocarbons could be used as a tracer for carbon monoxide. Carbon monoxide is dissipated rapidly from known sources, e.g., highways, in open areas. The contribution of combustion carbon monoxide to the total carbon monoxide is minimal ($\lesssim$5%) three miles downward.

SECTION III

RECOMMENDATIONS

The usefulness of this method for determining the sources and movement of carbon monoxide could be increased by taking samples simultaneously some distance apart. Air samples should be taken over a period of time at one location to determine movement of the pollutant plume from major metropolitan areas. An open area free of major sources of carbon monoxide as close to the city as possible would be desirable. A knowledge of the oxygen and carbon isotopic composition of carbon monoxide from other combustible materials would be useful in determining sources of carbon monoxide. An expansion of the diurnal studies would be useful in determining the balance of carbon monoxide in the atmosphere.

SECTION IV

EXPERIMENTAL PROCEDURES

The atmospheric samples were collected in ∿90 liter aluminum cylinders which had been evacuated by a mechanical pump connected through a liquid nitrogen trap. The cylinders were opened and allowed to come to atmospheric pressure and then pumped to 30 to 40# gauge with two rubber diaphragm compressors powered by a 12V battery. The intake port was ∿30 inches above the ground, and the sampling period was ∿15 minutes.

The air samples were processed according to the procedure of Stevens and Krout[3]. Briefly, the procedure is as follows: The sample is passed through a liquid N_2 trap and molecular sieves to remove moisture, CO_2, N_2O, NO, and NO_2; through Schutze reagent (I_2O_5) to oxidize the CO to CO_2; and through a liquid nitrogen trap to condense the CO_2 formed from the CO. The amount of CO_2 formed is measured manometrically and the isotopic ratios $^{13}C/^{12}C$ and $^{18}O/^{16}O$ are determined on a modified Consolidated-Nier Mass Spectrometer. The mass spectrometric procedure and calculations have been discussed by Stevens et al[1].

Additional air samples were taken in St. Louis in Tedlar plastic bags for CPL. For the first two St. Louis experiments, these samples were pumped just prior to the ANL samples. In the third experiment, the tanks were pumped and the plastic bags filled from the tanks so that identical samples would be analyzed by CPL and ANL.

The percent CO produced by combustion in any sample was calculated in the following manner:

$$\% \text{ combustion CO} = \frac{\delta(^{18}O/^{16}O)\ \text{sample} - \delta(^{18}O/^{16}O)\ \text{bkgd.}}{\delta(^{18}O/^{16}O)\ \text{air} - \delta(^{18}O/^{16}O)\ \text{bkgd.}}$$

The oxygen isotopic ratio for air, 23.5, relative to SMOW, reported by Kroopnick and Craig[4] was used in the above calculation.

SECTION V

EXPERIMENTAL CONDITIONS

On June 27, 1973, the wind was southwest at 0630. The upwind sample was taken southwest of Otto, Missouri, 29 miles southwest of St. Louis. By 0830 the wind was from the west. A sample of the urban air was taken at 12th and Clark at CAMP Station #1. Downwind samples, east of St. Louis, were taken near New Memphis, New Minden, and Carlyle, Illinois, respectively 31, 47 and 47 miles from the CAMP station. Consecutive samples were taken near New Minden, Illinois. Data are given in Table 1-A and conditions in Appendix A-1.

On July 17, 1973, the wind was southeast at 0600. The upwind sample was taken 18 miles southeast of St. Louis in an open field. At sampling time, the wind was light and from the east. The urban sample was taken at CAMP Station #1. Downwind samples were taken 25, 26, and 33 miles west of St. Louis. Data are given in Table 1-B and conditions in Appendix A-2.

Sample collection on October 25, 1973, was terminated after a 90° shift in the wind direction.

On November 13, 1973, with the wind out of the south, samples were taken periodically from 0630 to 1022 at a single location, 7.8 miles north of CAMP Station #1, in Bellefontaine. An upwind sample was taken late in the day southwest of Otto, Missouri. Data are given in Table 1-C and conditions in Appendix A-3.

On November 14, 1973, the wind was south-southeast, and a similar experiment was carried out. A sample further downwind was taken at 1030, 15.3 miles north of CAMP Station #1. Data are given in Table 1-D and plotted in Fig. 1. The conditions are given in Appendix A-3. Wind direction and speed for two nearby CAMP stations as well as the downtown station are given in Table 2.

Two experiments were carried out near Argonne, Illinois, along highway I-55 on July 31 and August 9, 1973. The wind was from the north at 8-10 mph on July 31 and from the west on August 9 at 10-12 mph. Traffic averaged 25 cars and 2 trucks per minute. Data are given in Table 3 and conditions in Appendix B.

A series of samples was taken over a 24-hour period on September 5 and 6, 1973, in a field of mature corn. The local roads were 0.5 mile to the south and 2 miles to the west with a minor highway 0.5 mile to the north. No cars passed on the road to the south during the night. The road to the west could not be seen. The wind was from the west at 5-8 mph and decreased during the night to 2-5 mph. The field was located 3.4 miles west of Plainfield, Illinois, ∿25 miles southwest of Argonne National Laboratory. The data are given in Table 4-A, the conditions in Appendix C-1 and plotted in Fig. 2.

Two replicate experiments were carried out at the same location in the early summer, shortly after the field was planted. On June 11, 1974, the wind was west at 8 mph early in the evening, but by midnight was light and variable and remained so until 0430 when the wind became 1-2 mph from the west-northwest. On July 18, 1974, the wind was out of the southwest at 5-8 mph. Sampling was discontinued when the wind shifted to north in the middle of the day. The data are given in Tables 4-B and 4-C; the conditions are given in Appendix C-2 and C-3. Wind direction and speeds as reported at ANL are given in Table 5.

SECTION VI

RESULTS AND DISCUSSION

In the attempts to sample the pollutant plume from St. Louis, Missouri, variable results were found. The June 27 effort covered an arc of 22° downwind, with the CO concentration and the $\delta(^{18}O/^{16}O)$ ratio decreasing along the arc. The CO concentration decreased likewise as the distance from the city increased. The decrease along the arc would appear to indicate that the plume maximum had passed the sampling point, assuming that the air mass moving from the city was being sampled. However, at the distance from the city and the reported wind speed of 5 mph, the plume would not have reached the sample point at sampling time.

The July 17 collection was made closer to the city with the plan that the plume would be more easily seen. The downwind sampling arc was only 12° with the contribution of urban CO in these samples less than 10%. At the reported wind speed the plume should have reached the sampling sites by the time the samples were taken. However, there had been an inversion earlier that morning which most probably delayed movement of the air mass over and from the city.

From the first two experiments it seemed that movement of the plume from the city might be detected if sequential air samples were taken downwind at a single location closer to the city center.

On November 13 and 14, 1973, at a location within the metropolitan St. Louis area, ~8 miles north of CAMP Station #1, air samples were taken during the morning from 0630. With the prevailing winds, the location was sufficiently far from freeways and arterial roads that CO produced thereon would have had, at the most, only a minimal effect (see below).

Although the wind was out of the south at the time sampling was begun and would have carried the plume over the sampling location, there was considerable variation in both the direction and speed of the surface winds during the sampling period on both days. During this time, the wind 300 feet above ground, as measured at CAMP Station #1, was steady with a much higher velocity, as is shown in Table 2. The inversion dissipated by 1000 each morning.

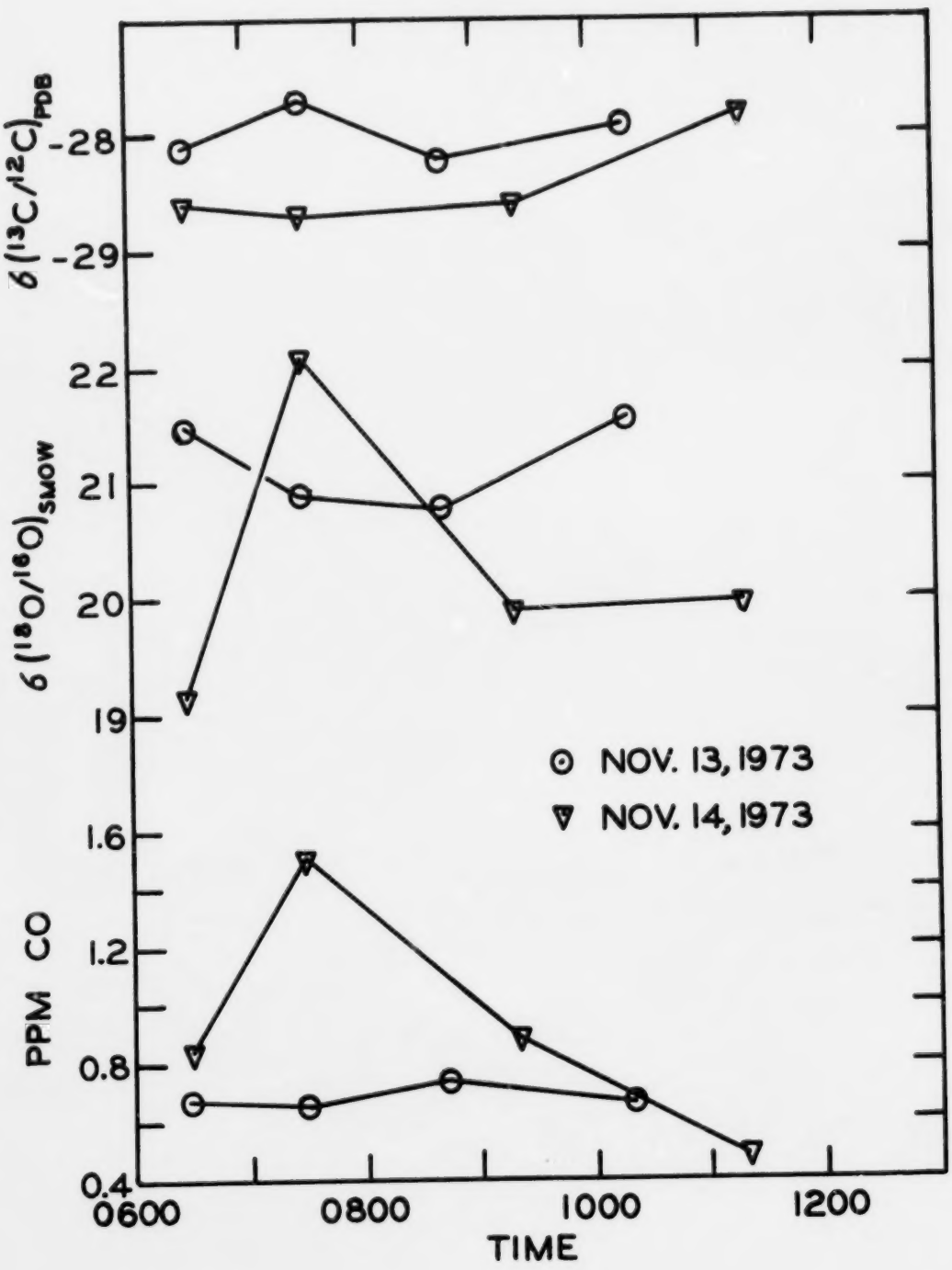

FIG. 1 PPM CO, $\delta(^{18}O/^{16}O)_{SMOW}$, and $\delta(^{13}C/^{12})_{PDB}$ VS. TIME IN ST. LOUIS, MISSOURI.

TABLE 1. Atmospheric Carbon Monoxide Concentrations and Isotopic Compositions for Samples Collected in St. Louis, Missouri

Sample No.	Time[a]	Sample Point: Distance Mi from St. Louis	Sample Point: Bearing Degrees	Wind: Speed (mph)	Wind: Directions Degreees	Concentration CO (ppm)	$\delta(^{13}C/^{12}C)$[b] (ppt)	$\delta(^{18}O/^{16}O)$[c] (ppt)
A. Sampled June 27, 1973								
1 (1)*	0740	29	220	5	225	0.20	-25.3	15.0[d]
2 (2)	0920	0	-	5	270	2.37	-28.9	23.3[d]
3 (3)	1310	31	113	5	270	0.41	-	-
4 (4)	1415	48	108	5	270	0.37	-28.7	16.7[d]
4a	1430	48	108	5	270	0.27	-26.3	17.1[d]
5 (5)	1510	46	86	5	270	0.21	-26.4	13.7
B. Sampled July 17, 1973								
1 (6)	0745	18	171	2	90	0.25	-26.5	14.4
2 (2)	0850	0	-	2.5	105	6.4	-28.5	22.3
3 (7)	1340	25	270	2.5	90	0.28	-27.5	14.8
4 (8)	1433	26	282	5	90	0.28	-28.6	14.9
5 (9)	1535	33	277	5	90	0.21	-27.2	13.8
5a (9)	1550	33	277	5	90	0.22	-27.3	14.2
C. Sampled November 13, 1973								
1 (10)	0630	7.8	348	10-12	180	0.68	-28.1	21.5
2 (10)	0730	7.8	348	12	160	0.66	-27.7	20.9
3 (10)	0845	7.8	348	8-10	160	0.75	-28.2	20.8
4 (10)	1022	7.8	348	8-10	200	0.67	-27.9	21.6
5 (1)	1830	29	220	5-8	247	0.22	-27.2	15.7
D. Sampled November 14, 1973								
6 (10)	0630	7.8	348	5	160	0.86	-28.6	19.2
7 (10)	0730	7.8	348	5-8	160	1.52	-28.7	22.1
8 (10)	0920	7.8	348	11	180	0.90	-28.6	19.9
9 (10)	1030	15.3	357	12	180	0.58	-27.9	20.6
10 (10)	1120	7.8	348	16	180	0.48	-27.8	20.0
E. Sampled July 25, 1973 (Plainfield, Ill.)								
1	1630	-	-	5-8	247	0.19	-28.5	13.7
Auto Exhaust 1973			-	-	-	-	-28.8	23.1

*Locations on Map D-1.

TABLE 1. (Con't.)

[a]Denotes starting time - sampling period - 15 minutes.

[b]δ $^{13}C/^{12}C$) is the relative difference in parts per thousand (ppt) between the $^{13}C/^{12}C$ ratio calculated from mass spectrometric data and the accepted value of the same ratio for the carbon isotopic standard, Peedee belemnite. The normal external error is ±0.3 ppt for $\delta(^{13}C/^{12}C)$.

[c]$\delta(^{18}O/^{16}C)$ SMOW - is the relative difference in parts per thousand (ppt) between the $^{18}O/^{16}O$ ratio calculated from mass spectrometric data and the accepted value of the same ratio for the oxygen isotopic standard, mean ocean water. The normal external error is ±0.5 ppt for $\delta(^{18}O/^{16}O)$.

[d]These values may be high by as much as one part per thousand.

TABLE 2. Wind Direction, Wind Speed and CO Concentration for Three St. Louis County Air Monitoring Stations(1)

Time	1*			5**			8***		
	WD	WS mph	CO ppm	WD	WS mph	CO ppm	WD	WS mph	CO ppm
Nov. 13, 1973									
0400-0500	191	23	1.2	-	-	0.6	170	1.6	1.2
0500-0600	189	22	1.4	-	-	0.5	140	3.5	3.1
0600-0700	192	22	1.9	-	-	0.7	165	3.0	3.4
0700-0800	179	18	2.4	-	-	1.2	149	4.8	3.8
0800-0900	180	21	2.9	-	-	1.0	146	8.0	3.9
0900-1000	199	21	2.0	-	-	0.9	198	4.8	3.9
1000-1100	202	18	-	-	-	0.8	204	5.7	3.6
Nov. 14, 1973									
0400-0500	203	15	2.7	-	-	0.7	183	1.5	4.6
0500-0600	190	15	3.4	-	-	0.6	151	1.9	4.6
0600-0700	192	13	4.9	-	-	0.6	150	3.8	5.0
0700-0800	185	14	5.9	-	-	1.1	151	2.5	5.9
0800-0900	174	15	4.2	-	-	1.2	144	6.5	5.7
0900-1000	198	18	5.2	-	-	0.8	166	4.7	5.2
1000-1100	208	26	4.8	-	-	1.4	198	5.1	5.1
1100-1200	200	27	4.9	-	-	0.8	190	5.4	5.0

*Station 1 - Civil Courts Bldg. and instruments on 10' tower on roof >300' above street. CO instrument at 12th and Clark.

**Station 5 - On flood plain, near waterworks.

***Station 8 - Routes 67 and 270, Bellefontaine State Farm. Wind instruments on tower 20' above ground.

(1) Data courtesy of J. Clark, St. Louis County, Air Monitoring Program.

Thus, it is not likely that the plume would have been detected either morning for the movement of air was variable and not across the city, as expected. The samples show a decided increase in the CO level which is three to four times that found in rural locations. From the oxygen isotopic ratios it is estimated that 70-80% of the CO is from combustion sources. The maximum found in the 0730 sample for November 14 for both the CO concentration and the oxygen isotopic ratios corresponds to maxima found in the CO concentration for CAMP Stations 1 and 8. This increase appears to be the morning maximum that was expected to move out from the city and could be detected as it moved away from the city. On this day it appeared to form and accumulate in the city until the inversion cleared, for the sample, taken at 1030, November 14, ∿15 miles downwind in a rural area showed a significant proportion of urban air. The CO concentration was ∿2.5 times that normally found in rural areas, and the contribution of CO from combustion sources was estimated to be ∿70%. In view of these results, it would have been desirable to have taken the day's samples at this location for it appeared that urban air was reaching this area and the plume would have been detected as it moved out from the city.

Two experiments were carried out on July 31 and August 9, 1973, to evaluate the dispersion of CO from a major highway to determine the extent to which a localized source of CO would influence the composition and concentration of CO associated with a large air mass such as that of the St. Louis area. Since a highway is a linear source and does not have a plume in the sense that a point source does, the CO concentration gradient at ground level due to dispersion should only be transverse to the highway.

The first experiment was carried out along an east-west stretch of Interstate 55, thought to be sufficiently west of Chicago to be free of urban air, with a north wind blowing. The second experiment utilized a north-south stretch of I-55 with a west wind.

Althoug the air mass for the first experiment appears to have been heavily contaminated with urban air, the effect of the combustion source of the CO is evident only in the near vicinity of the highway. The

TABLE 3. Atmospheric Carbon Monoxide Concentrations and Isotopic Compositions for Dispersion Study Along I-55

Sample No.	Time	Distance Miles	Wind Speed	Wind Direction	Concentration CO (ppm)	$\delta(^{13}C/^{12}C)$	$\delta(^{18}O/^{16}O)$ (SMOW)
			A. Samples Collected July 31, 1973				
1 (1)*	0940	0.8 N	8-10	30°	0.55	-28.1	21.1
2 (2)	1000	0	"	"	1.31	-28.0	23.0
3 (3)	1020	0.5 S	"	"	0.60	-28.0	19.9
4 (4)	1040	1.5 S	"	"	0.55	-27.7	20.6
5 (5)	1117	3.5 S	"	"	0.50	-27.8	19.1
			B. Samples Collected August 9, 1974				
1 (6)	1700	3.3 W	10-12	240-270°	0.15	-27.9	11.5
2 (7)	1733	0	"	"	0.72	-28.0	21.6
2a	1733	Duplicate pumped at the same time			0.70	-28.0	21.6
3 (8)	1800	0.5 E	"	"	0.19	-28.1	15.2
4 (9)	1823	2.0 E	"	"	0.16	-28.6	12.6

*Locations on Map D-2.

effect is the same in the second experiment, only more pronounced because of the uncontaminated nature of the air mass. The air sampled at 0.5 and 2 miles downwind is estimated to contain 31% and 9%, respectively, of combustion CO. It appears from these data that air samples taken at least three miles from major roads would contain a negligible amount of engine CO.

The diurnal studies of September 5-6, 1973, were conducted in a field of mature corn to determine the nature of any changes in the CO concentration and isotopic ratios in a rural atmosphere. The area was free of localized sources of CO and the wind conditions (W, SW) were chosen so that contamination by auto CO was minimal.

During the night, the CO concentration varied inversely with the $\delta(^{18}O/^{16}O)$ and $\delta(^{13}O/^{12}O)$ ratios. This effect suggests that the lighter CO is being preferentially scavenged by a process such as the soil microorganism consumption studied by Inman et al[5]. Although Inman reports a substantial temperature effect in the rate of absorption, this would affect the overall process very little. During the night, the rate of natural CO production as well as combustion CO should be greatly decreased allowing this absorption-fractionation process to be seen.

If fractionation is occurring, the change in the oxygen isotopic ratio would be expected to be twice that of the carbon isotopic ratio and a plot of these ratios would have a slope of two. In this plot, the data for the night samples of September 5-6, 1973, show a close approximation to a slope of two, and one is tempted to conclude that fractionation is occurring. However, there is not sufficient data to conclusively demonstrate this.

The conditions for the other two diurnal studies on June 11 and July 18, 1974, were not ideal. There was an inversion the night of June 10 and the winds were light and variable. On July 18, the winds were strong and had been out of the southwest for a relatively short time. There was also a smell of wood smoke in the air although no fire or smoke could be seen. On both nights, the CO concentration was nearly twice that of the normal rural value, indicating contaminated air.

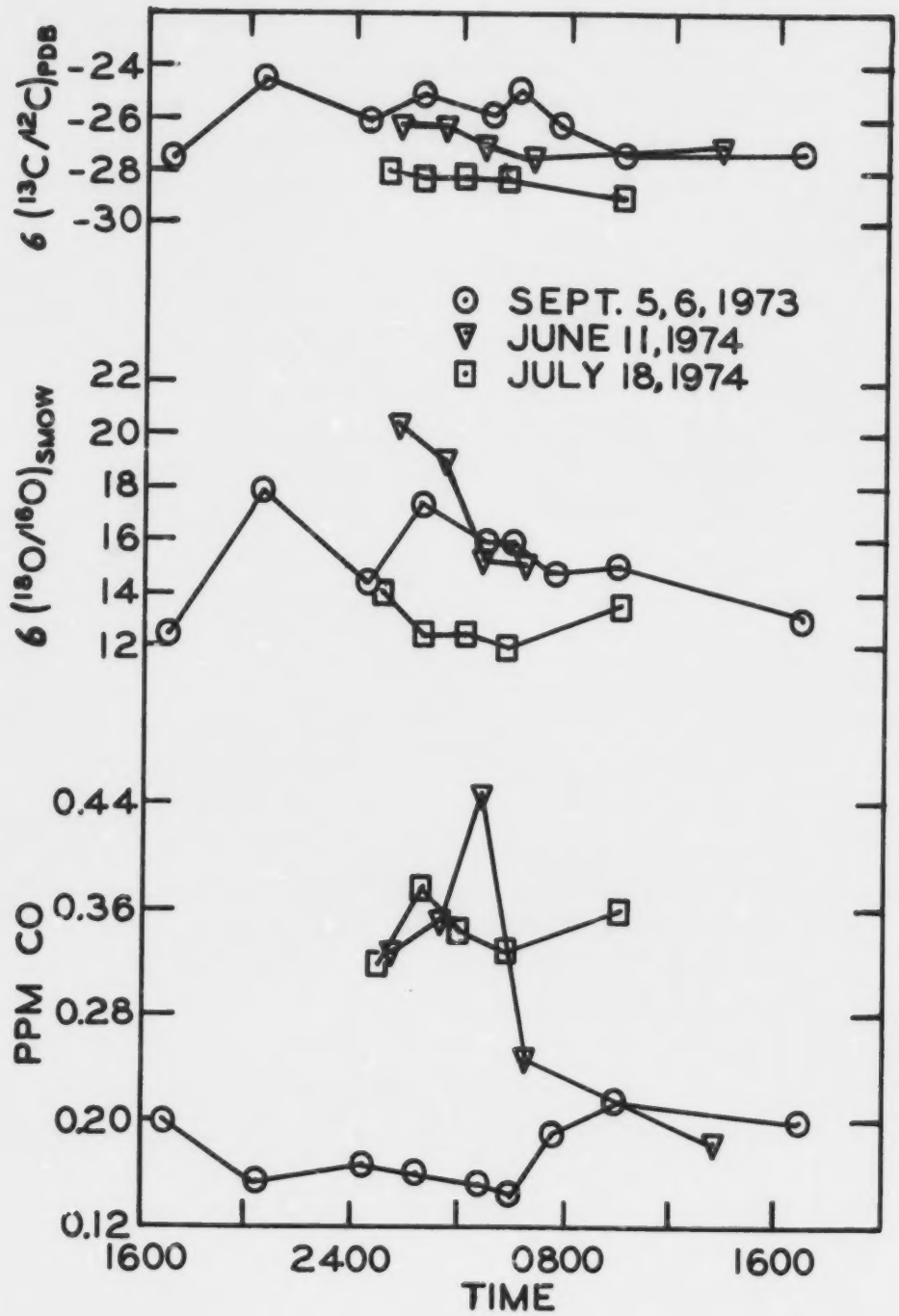

FIG. 2 DIURNAL STUDIES, PPM CO, $\delta(^{18}O/^{16}O)_{SMOW}$, AND $\delta(^{13}C/^{12}C)_{PDB}$ VS. TIME.

TABLE 4. Atmospheric Carbon Monoxide Concentrations and Isotopic Composition for Diurnal Studies, Plainfield, Illinois

Sample No.	Time	Wind Speed (mph)	Wind Direction Degrees	CO Concentration (ppm)	$\delta(^{13}C/^{12}C)$	$\delta(^{18}O/^{16}O)$
			A. Sampled September 5 and 6, 1973			
1*	1655	5-8	290	0.20	-26.5	12.4
2	2030	2-5	280	0.14	-24.5	17.9
3	0030 (9/6)	"	300	0.16	-26.1	14.4
4	0230	"	280	0.15	-25.1	17.5
5	0500	"	290	0.14	-25.9	15.9
6	0600	"	290	0.13	-24.8	16.0
7	0730	"	300	0.19	-26.2	14.8
8	1001	4-8	315	0.22	-27.3	15.1
9	1655	3-5	290	0.20	-27.2	13.0
			B. Sampled June 11, 1974			
1	0130	light and variable		0.36	-26.3	20.5
2	0315	calm		0.39	-26.3	19.0
3	0445	1-2	315	0.51	-27.0	15.3
4	0635	1-2	225	0.26	-27.5	15.1
5	1345	15-20	270	0.18	-27.0	-
			C. Sampled July 18, 1974			
1	0055	5-7	225	0.35	-28.0	14.0
2	0230	8-10	"	0.42	-28.3	12.4
3	0355	5-8	"	0.38	-28.2	12.4
4	0540	8-10	"	0.36	-28.3	12.0
5	0950	5-7	"	0.40	-29.0	13.5
			D. Sampled June 13 and July 9, 1974			
1	1300	4-10	250	0.19	-26.0	10.7
2	1410	4-10	240-290	0.18	-26.0	11.6
3	1220 (7/9)	5-10	270	0.20	-30.6	10.3
			E. Sampled July 25, 1973			
1	1630	5-8	250	0.19	-28.5	13.7
2	1645	8-10	250	2.46	-24.1	36.8

*All samples - Location 10, Map D-2.

TABLE 5. Wind Direction and Wind Speed
June 10, 11 and July 17, 18, 1974
Argonne Illinois

Time	WD	WS
June 10, 1974		
0800	230	16
1000	240	17
1400	290	18
1800	300	13
2100	310	3
2400	light and variable	
June 11, 1974		
0100	230	1
0300	130	0.5
0500	170	1
0700	120	2
0900	260	8
July 17, 1974		
0300	180	4
0600	220	3
0900	230	5
2400	270	8
July 18, 1974		
0100	230	8
0300	240	10
0600	230	11
0900	240	4
1200	320	4
1300	180	3

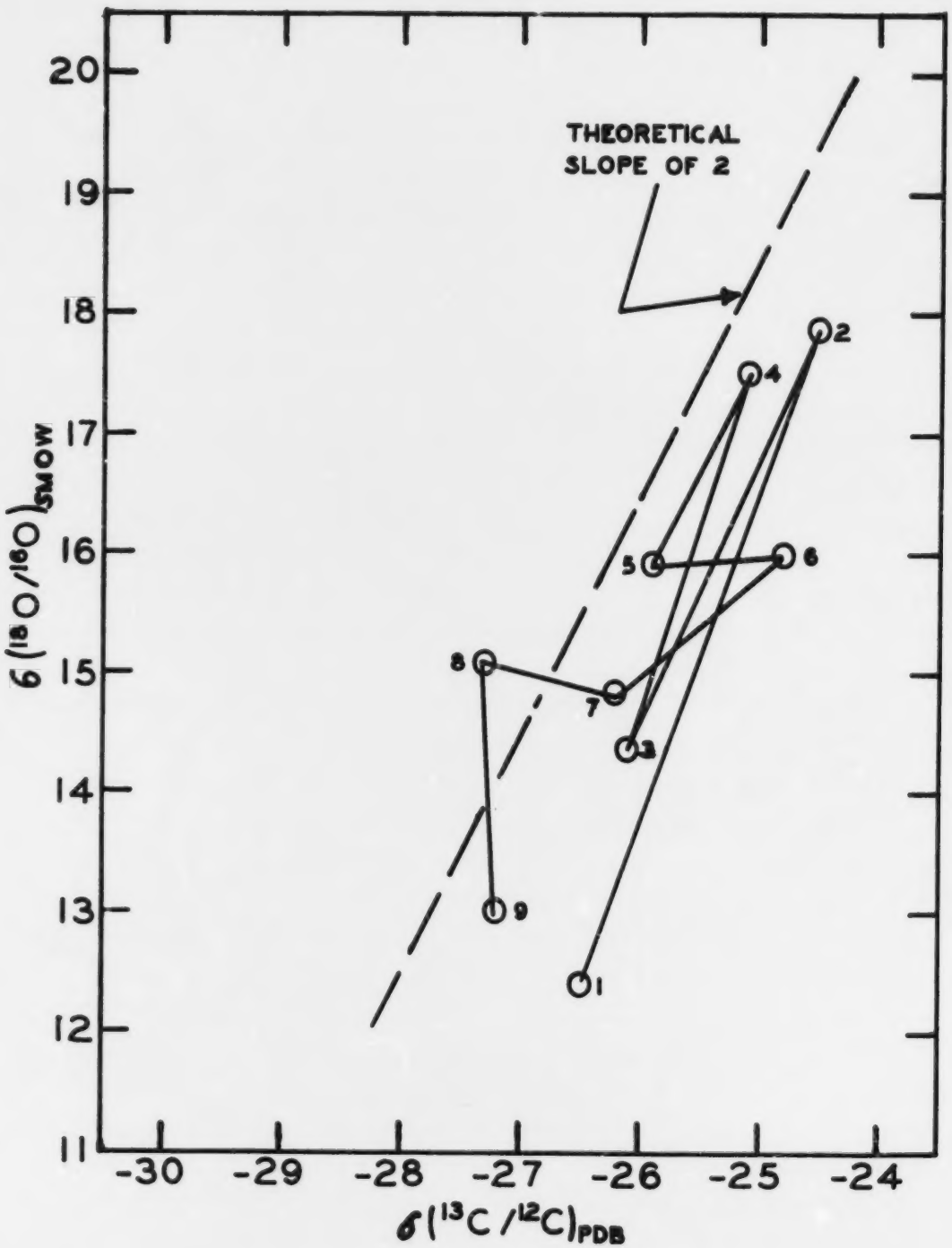

FIG. 3 OXYGEN VS. CARBON ISOTOPIC RATIOS FOR DIURNAL STUDY, SEPTEMBER 5,6, 1973.

It can be seen in the data for June 11, when the winds changed to the southwest and the inversion cleared, the CO value dropped to that expected for rural air.

The oxygen isotopic ratios for the samples taken June 11 indicate that approximately 70% of the CO is of combustion origin. This seems likely in view of the inversion and the light winds which would tend to hold the products of combustion in the area. Although the CO concentrations for the samples of July 18 are about the same as those for the previous experiment, the oxygen isotopic ratios are lower and indicate that 10 to 20% of the CO is due to fossil fuel combustion. The reason for the lower oxygen isotopic ratios with that level of CO in the latter case is not obvious. This effect may be due to other non-fossil fuel combustion sources of CO.

All the diurnal experiments show a difference in the behavior of CO between night and day. During the night, the oxygen isotopic ratios change inversely to the change in the CO concentration. During the day, these values change in a parallel manner. This is also true for the carbon isotopic ratios, but to a lesser extent.

It would appear that the oxygen isotopic ratio is a sensitive indicator of fossil fuel combustion for, as can be seen from the diurnal experiments, with the coming of day, as the amount of CO increases so does the oxygen isotopic ratio. This may indicate that the residence time of CO in the atmosphere is less than has been previously estimated[1,6,7].

To observe the fractionation effects is not easy. There is the steady movement of air as well as the daily and seasonal variation in production of CO. Stevens et al[1] saw little, if any, evidence of fractionation for a large number of samples taken over a 15-month period. These samples were taken primarily at the same time of day (3 to 5 p.m.) when it would appear from the data presented here that combustion CO predominates and would obscure any fractionation effects.

It was hoped that some easily or conveniently analyzed pollutant would serve as a tracer for the plume, e.g., SO_2, NO_2. No instruments were immediately available for this. However, the possibility of tracing with hydrocarbons was considered, and the data of CPL are included

here in Tables 6 and 7. In Tables 8 and 9, the ratio of the CPL hydrocarbon (HC) values to the CPL CO concentrations are given. For the samples pumped separately from the ANL samples, the ratios are not as consistent for each component, as the ratios are for the samples taken from the ANL tanks. There is, however, a noteworthy consistency for the HC/CO ratios of the latter samples. This may have been due to the higher HC levels in the latter samples. It would appear from the available data that these ratios might be used to spot a malfunction of equipment or a poor sample.

To determine if there might be a useful relationship between the hydrocarbons and CO, the CPL data for the HC has been plotted vs. the CO concentration in Figs. 4-12. For some of the HC, i.e., methane, ethylene, n-, i- and cyclopentane, their concentration is proportional to the CO concentration for all samples, both rural and urban, summer and fall. For ethane and propane there appears to be a difference between the summer and fall samples. For acetylene, propylene, n- and i-butane there appears to be a difference between urban and rural samples.

It would be expected that the concentration of these hydrocarbons would be proportional to the CO concentration since a number of them, i.e., ethylene, methane, propylene, and acetylene, have been reported by Hurn[8] as the prinicpal constituents of engine exhaust and this is confirmed for ethylene and methane and for the urban samples of acetylene and propylene.

The most interesting of these hydrocarbons is methane in that most of the points, summer and fall, rural and urban, fell along the curve. In these samples, the methane concentration varies only by a factor of 2 while the CO concentration varies by a factor of $\sim$20. The curve extrapolates to a background value of $\sim$1.4 ppm which agrees quite well with the reported values for atmospheric methane of 1.2 ± 0.2 ppm[9]. This is further indication that there are natural sources of methane greater than engine exhaust. The oil fields, which are one possible source, may account for the two high values of rural samples, since these samples were taken in an area which has producing oil wells. The reason for low values of the two summer urban samples, June 27

TABLE 6

Hydrocarbon Analyses of Atmospheric Samples
Collected in St. Louis, Missouri, June 27 and July 17, 1973

CONCENTRATION IN ppb (Vol./Vol.)*

	June 27					July 17				
Compound	1	2	3	4	5	1	2	3	4	5
Ethane	5.3	11.6	7.8	6.7	4.3	9.3	25.8	5.2	4.9	4.5
Ethylene	7.6	27.4	7.6	11.8	4.7	7.3	85.4	4.3	3.5	7.6
Propane	4.0	10.3	8.4	6.0	1.9	14.6	25.1	5.0	4.6	4.2
Acetylene	1.0	18.3	4.1	3.5	1.9	11.9	80.3	2.5	2.7	1.1
Isobutane	1.1	14.2	4.1	2.7	2.1	15.2	41.2	1.5	1.9	0.9
n-Butane	3.5	65.0	13.0	10.3	2.3	10.7	100.9	6.0	5.7	3.0
Propylene	2.3	8.9	1.5	1.2	1.0	0.3	29.9	1.7	1.9	0.6
Propadiene										
Neopentane										
Isopentane	5.7	86.8	12.3	9.8	†NM	11.6	146.2	6.8	5.8	3.4
n-Pentane + Cyclopentane	4.4	57.0	8.0	7.9	†NM	6.6	66.3	3.2	3.1	2.3
1-Butene										
2-Methyl-Propene										
Trans-2-Butene										
Non Methane HC (FIA)										
Methane	1200.	1320.	1600.	2430.	2180.	1700.	2650.	1660.	1690.	1620.
Carbon Monoxide	230.	1200.	500.	620.	430.	320.	5700.	370.	380.	260.

†Not Measurable

*Analyses by Chemistry and Physics Laboratory, EPA.

TABLE 7

Hydrocarbon Analyses of Atmospheric Samples
Collected in St. Louis, Missouri, November 13 and 14, 1973

CONCENTRATION IN ppb (Vol./Vol.)*

Compound	November 13				November 14				
	1	2	3	4	6	7	8	9	10
Ethane	19.0	16.5	18.8	21.5	34.4	42.5	25.3	20.1	19.2
Ethylene	11.0	9.0	11.6	11.1	13.7	24.5	13.0	9.1	7.3
Propane	17.1	22.6	23.4	19.7	54.5	107.8	33.0	16.6	13.1
Acetylene	9.8	9.1	9.1	9.1	9.6	17.6	11.0	7.9	4.8
Isobutane	8.5	7.6	12.4	8.6	21.5	19.8	13.4	9.1	5.6
n-Butane	24.7	23.7	47.9	24.4	35.2	64.8	40.4	26.0	20.2
Propylene	3.3	3.6	4.0	3.5	28.0	9.6	3.8	2.5	21.0
Propadiene									
Neopentane									
Isopentane	5.7	16.1	26.3	18.0	22.5	40.1	25.7	16.5	11.8
n-Pentane + Cyclopentane	0	9.3	12.5	10.4	13.1	20.9	13.6	8.8	6.4
1-Butene									
2-Methyl-Propene									
Trans-2-Butene									
Non Methane HC (FIA)									
Methane	1845.	1737.	1737.	1880.	2166.	2321.	1830.	1736.	1786.
Carbon Monoxide	551.	566.	646.	630.	743.	1211.	760.	517.	428.

*Analyses by Chemistry and Physics Laboratory, EPA.

TABLE 8

Ratios of Hydrocarbon to Carbon Monoxide Concentrations
for Samples Collected June 27 and July 17, 1973

1. Samples Collected June 27 and July 17, 1973:

ppb HC/ppm CO

	6/27					7/17				
Compound	1	2	3	4	5	1	2	3	4	5
Ethane	23	10	16	11	10	29	4	14	13	17
Ethylene	33	23	15	19	11	23	15	12	9	14
Propane	17	9	17	10	4	46	4	14	12	16
Acetylene	4	15	8	6	4	37	15	7	7	4
i-butane	5	12	8	4	5	48	7	4	5	4
n-butane	15	54	26	17	5	33	18	16	15	12
Propylene	10	7	3	2	2	1	5	5	5	2
i-Pentane	25	72	25	16	-	36	26	18	15	13
n-Pentane + Cyclopentane	19	48	16	13	-	21	12	9	8	9
Methane (ppm/ppm CO)	5.22	1.10	3.20	3.92	5.07	5.31	0.465	4.49	4.45	6.23
CO ppb	230	1200	500	620	430	320	5700	370	380	260

TABLE 9

Ratios of Hydrocarbon to Carbon Monoxide Concentrations for Samples Collected November 13 and 14, 1973

	ppb HC/ppm CO								
	November 13				November 14				
Compound	1	2	3	4	6	7	8	9	10
Ethane	35	29	29	34	46	35	33	39	45
Ethylene	20	16	18	18	18	20	17	18	17
Propane	31	40	36	31	73	89	43	32	31
Acetylene	18	15	14	14	13	14	14	15	11
i-Butane	15	13	19	14	29	16	18	18	13
n-Butane	45	42	74	39	47	54	53	50	47
Propylene	6	6	6	6	4	8	5	5	5
i-Pentane	10	28	41	28	30	34	34	32	28
n-Pentane + cyclo-pentane	-	16	19	16	18	17	18	17	15
Methane (ppm/ppm CO)	3.35	3.07	2.67	2.98	2.92	1.92	2.41	3.36	4.17
CO ppb (ACL)	551	566	646	630	743	1211	760	517	468
CO ppb (ANL)	680	656	747	674	858	1524	901	576	485
Ratio ACL/ ANL	0.81	0.86	0.86	0.93	0.87	0.79	0.84	0.90	0.88

and July 17, is not obvious. However, all the HC values of sample #2, July 17, except that of acetylene, fall below the respective curves.

It would seem then that either methane or ethylene could be used as a tracer for CO, given a portable instrument.

There are some apparent anomalies in the HC/CO ratios, i.e., samples 6 and 7 for propane, sample 6 for i-butane and sample 3 for n-butane on November 13-14, 1973; and sample 2 on June 27, 1973, for n-butane, i-pentane and n-pentane plus cyclopentane. These ratios are high and the original values should probably be rejected.

Also included is a ratio of the CPL/ANL values for the CO concentration. There appears to be a consistent bias. At this point, it is not known whether it is due to bag permeability to CO, instrumental problems, calibration, or some other factor.

With the natural sources of CO still uncertain, an isolated and unrepeated occurrence is noted as possibly having some bearing on the natural production of CO.

Unusual values for the oxygen and carbon isotopic ratios were found one afternoon when consecutive samples were taken near Plainfield, Illinois. The first sample was taken with the temperature at 90°F and the sky overcast. During the pumping of the second sample, the cloud cover and wind speed increased with a thunderstorm 3-10 miles upwind, and the temperature dropped abruptly to 82°F. Both the oxygen and carbon isotopic ratios increased markedly. O'Neil and Epstein[10] noted a marked changed in the oxygen isotope ratios of water vapor and rain with the approach and passage of a cold front. The oxygen isotopic ratio decreased in that case, however. The experiment was not repeated because the conditions did not occur again during the course of this study. The results are given in Table 3.

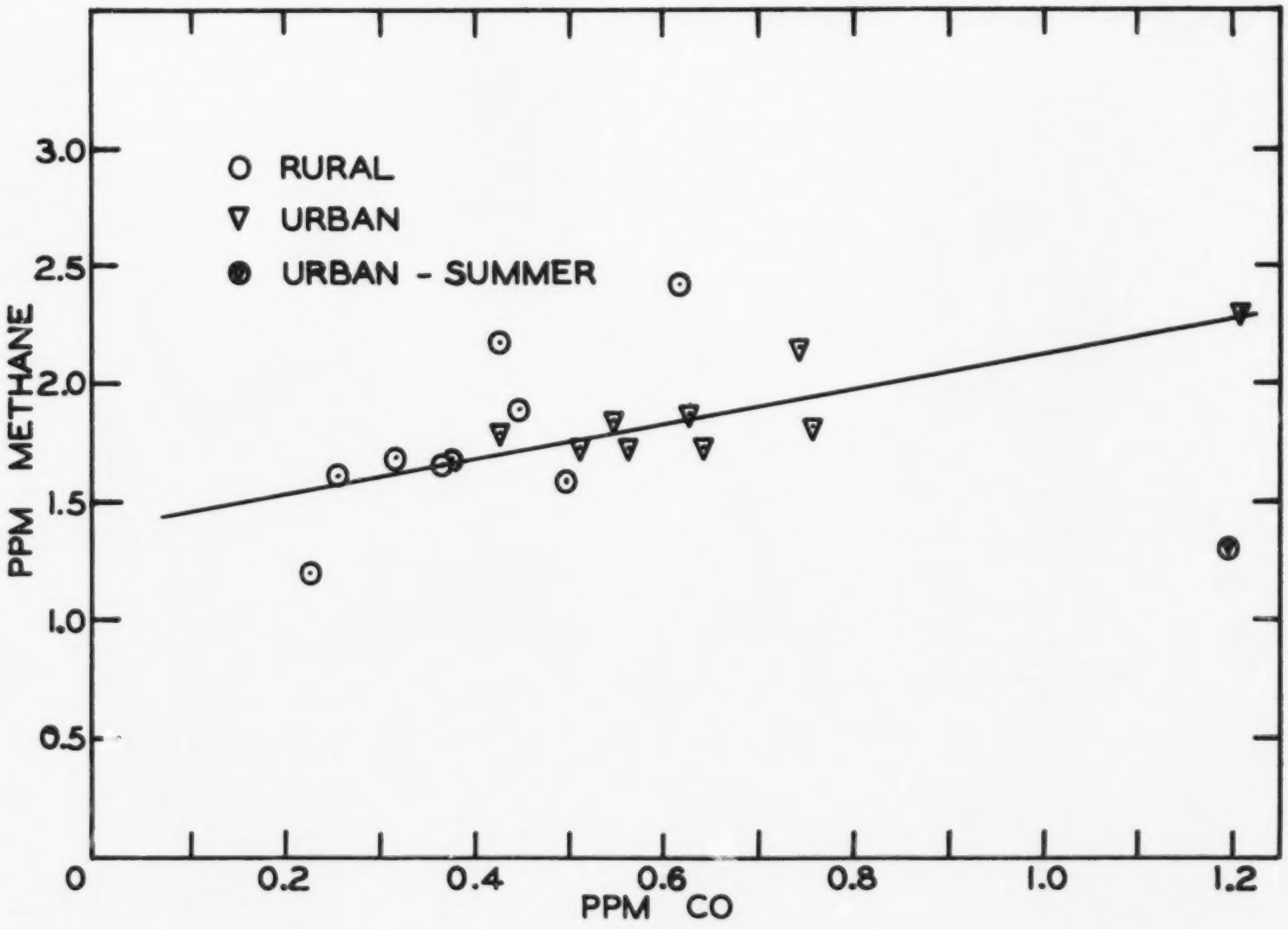

FIG. 4 PPM METHANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

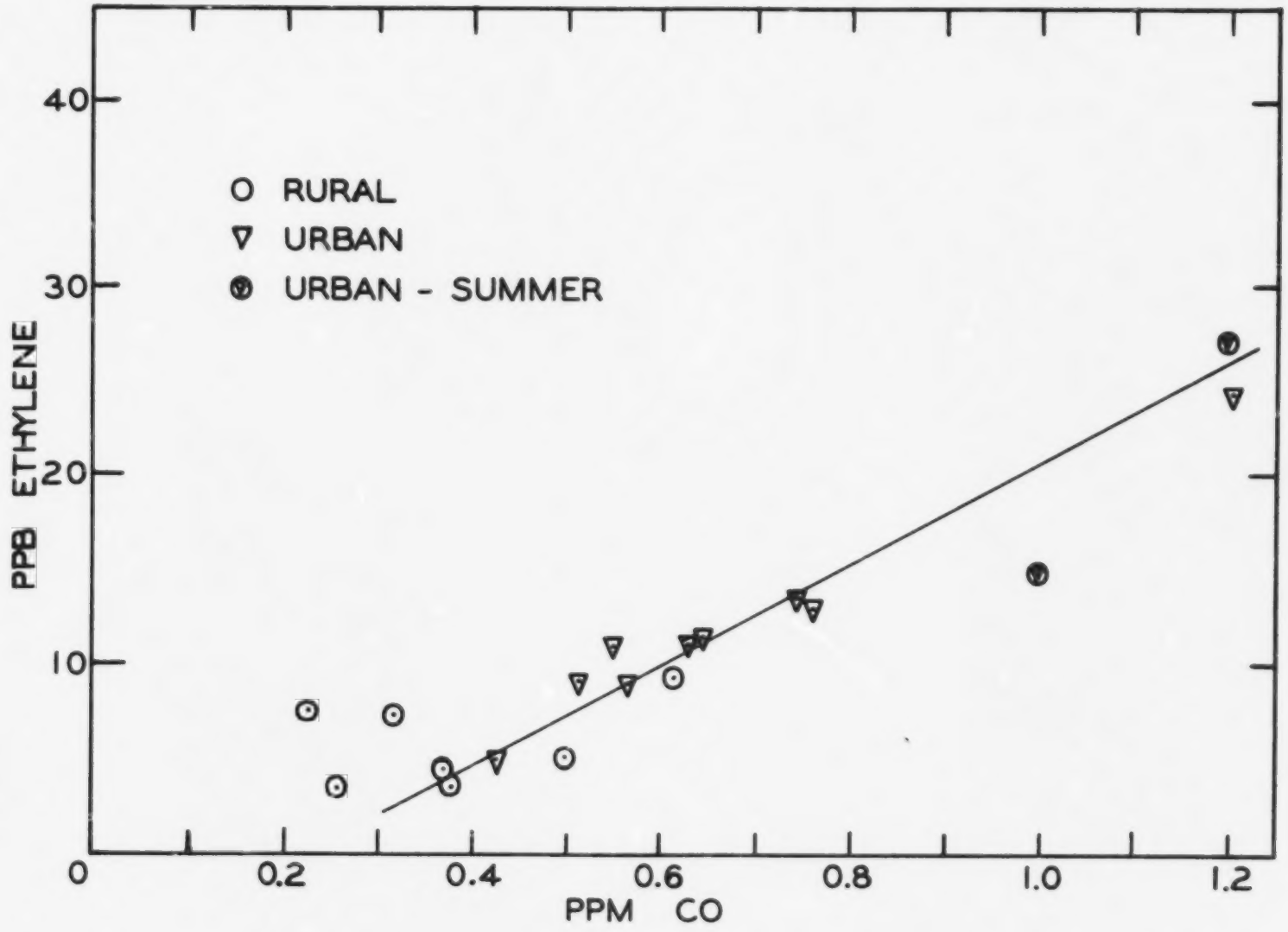

FIG. 5 PPB ETHYLENE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

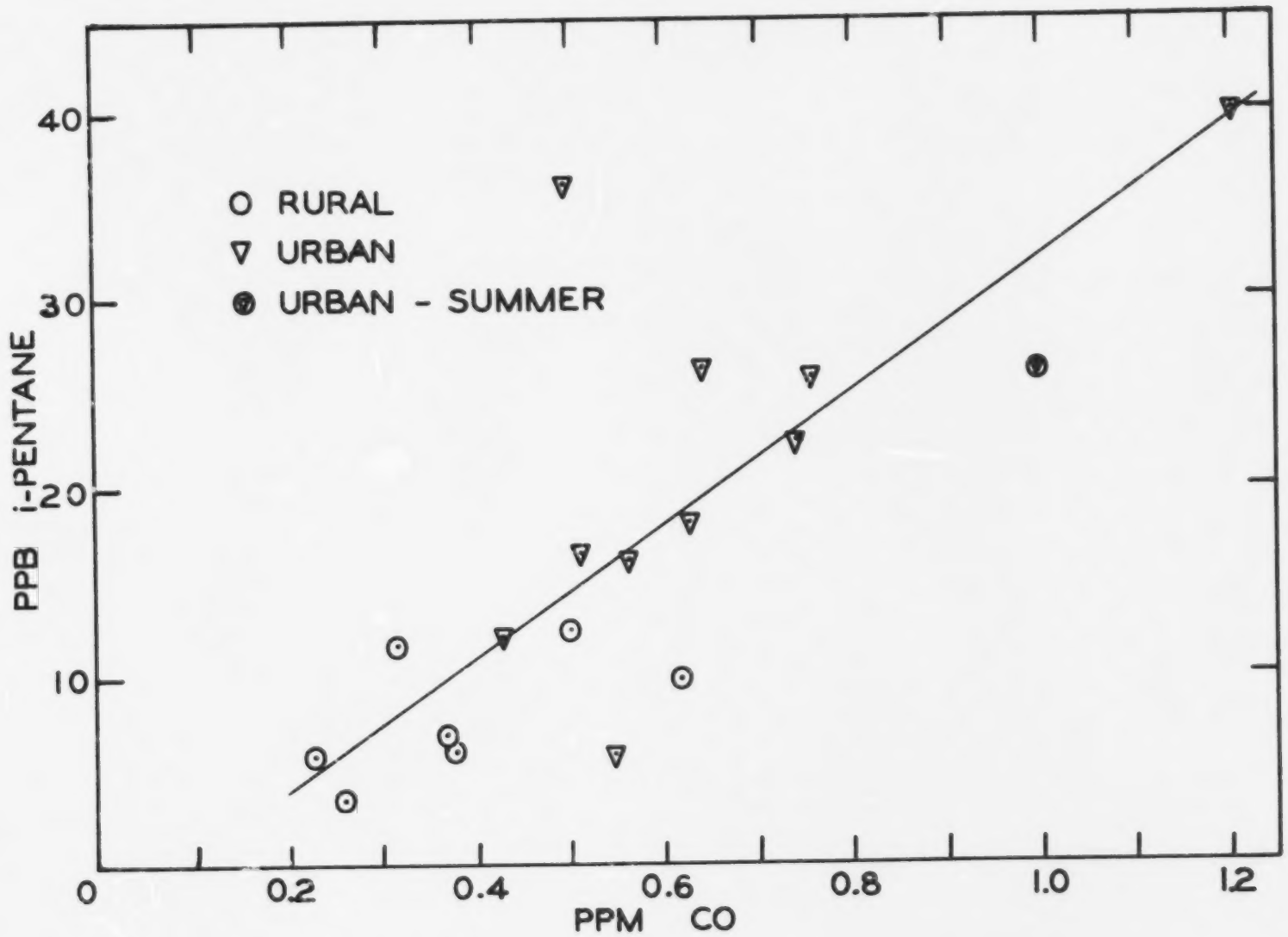

FIG. 6 PPB i-PENTANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

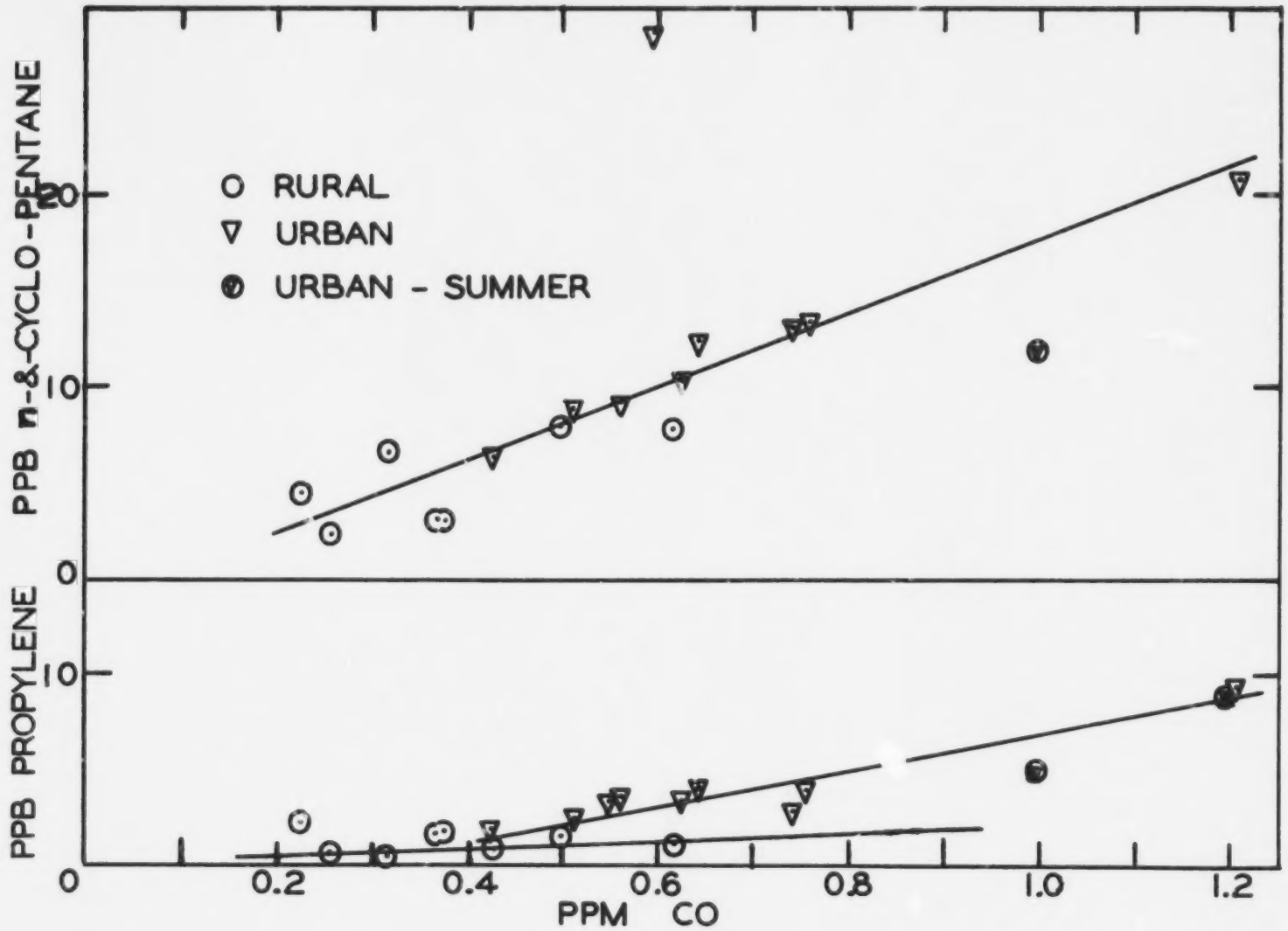

FIG. 7A, 7B PPB n- AND CYCLO-PENTANE AND PROPYLENE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

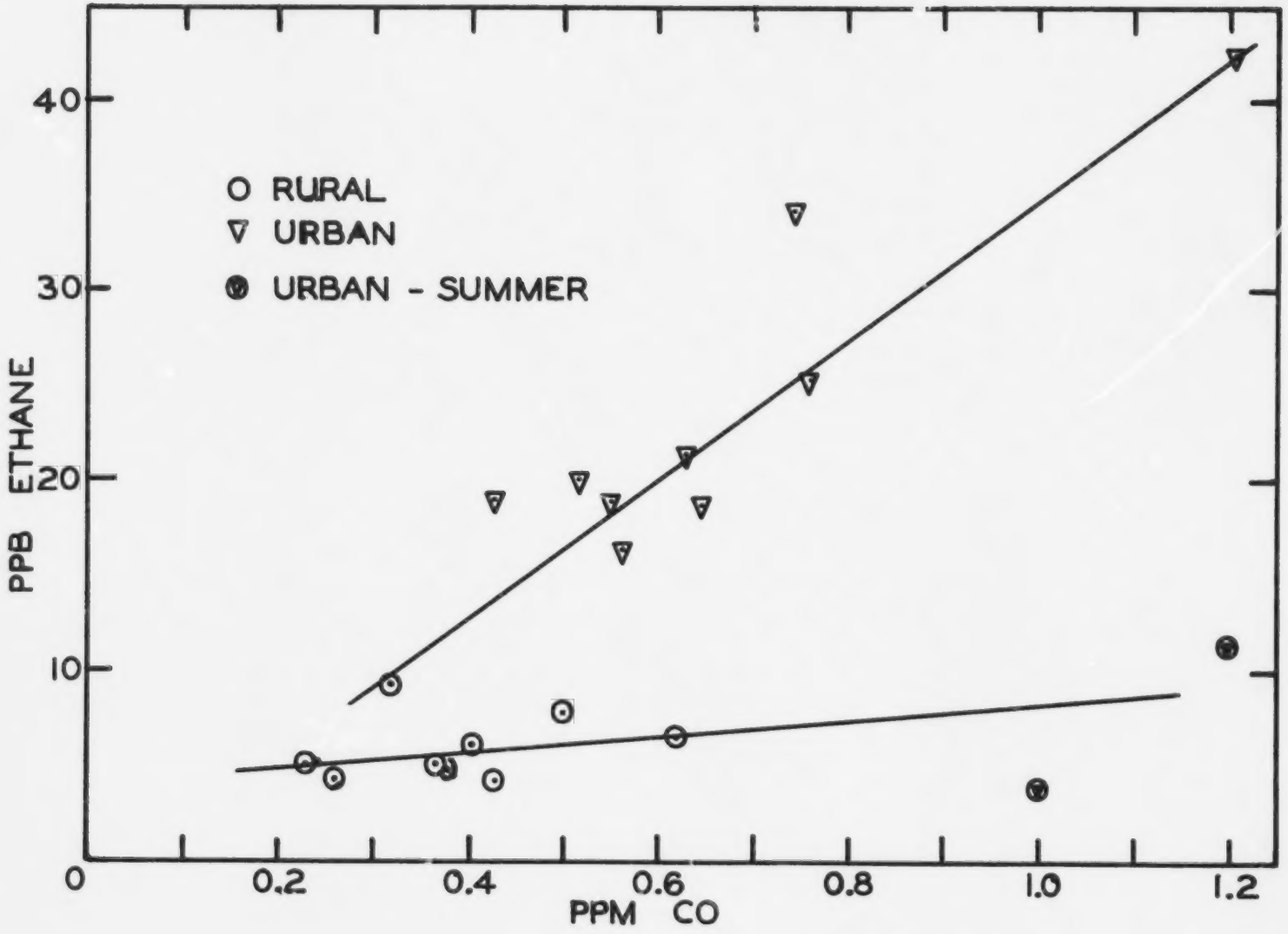

FIG. 8 PPB ETHANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

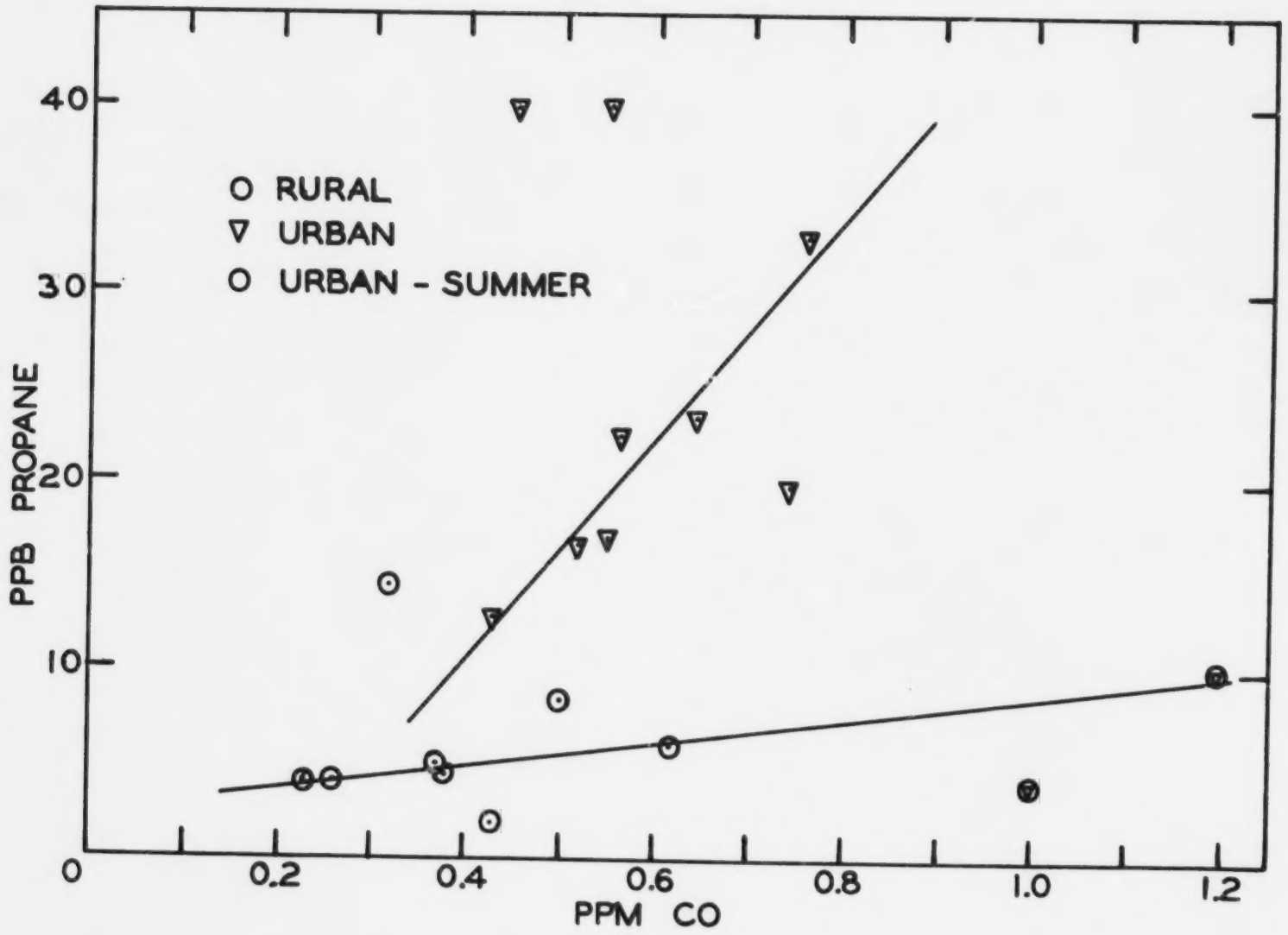

FIG. 9 PPB PROPANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

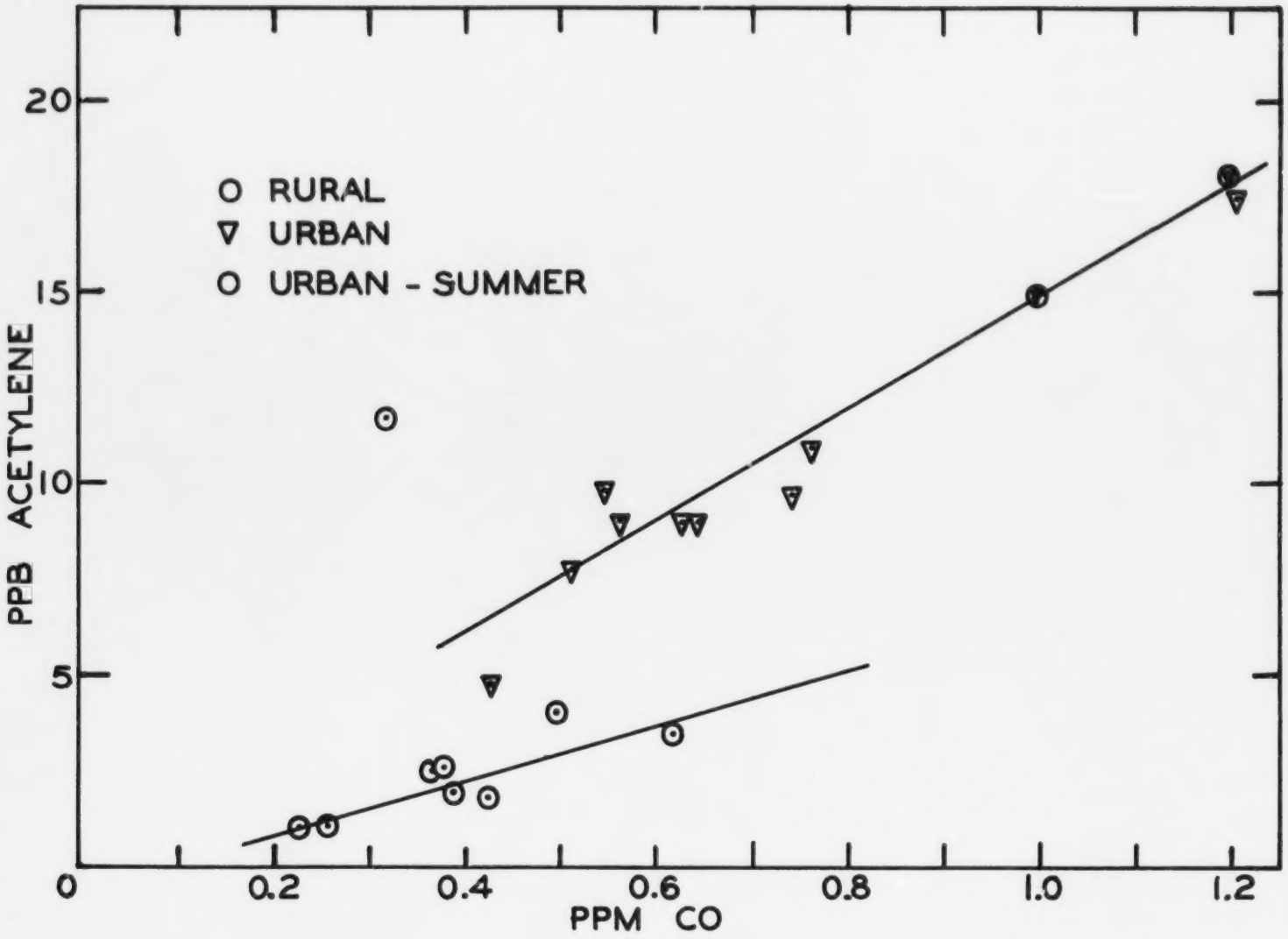

FIG. 10 PPB ACETYLENE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

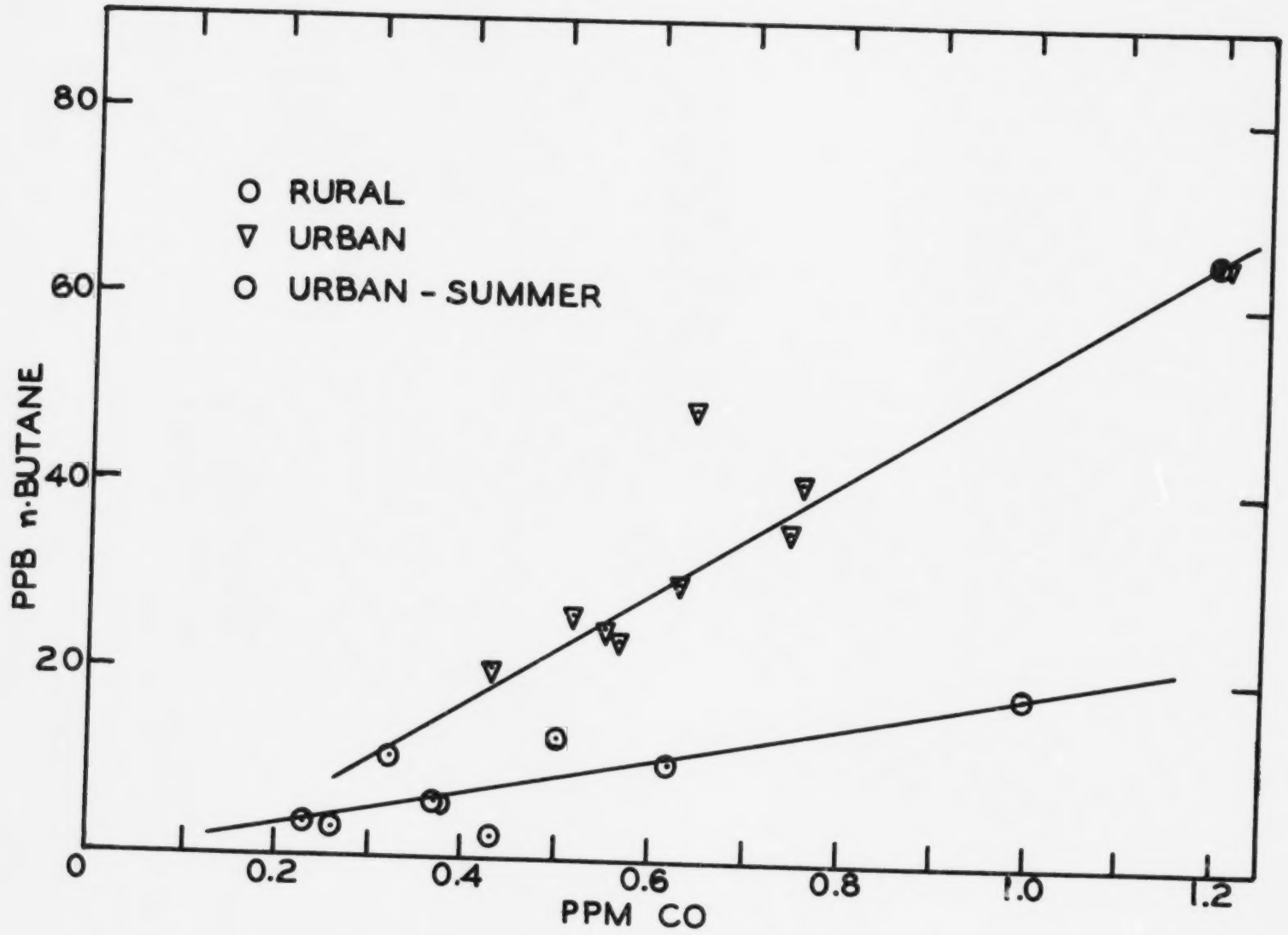

FIG. 11 PPB n-BUTANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

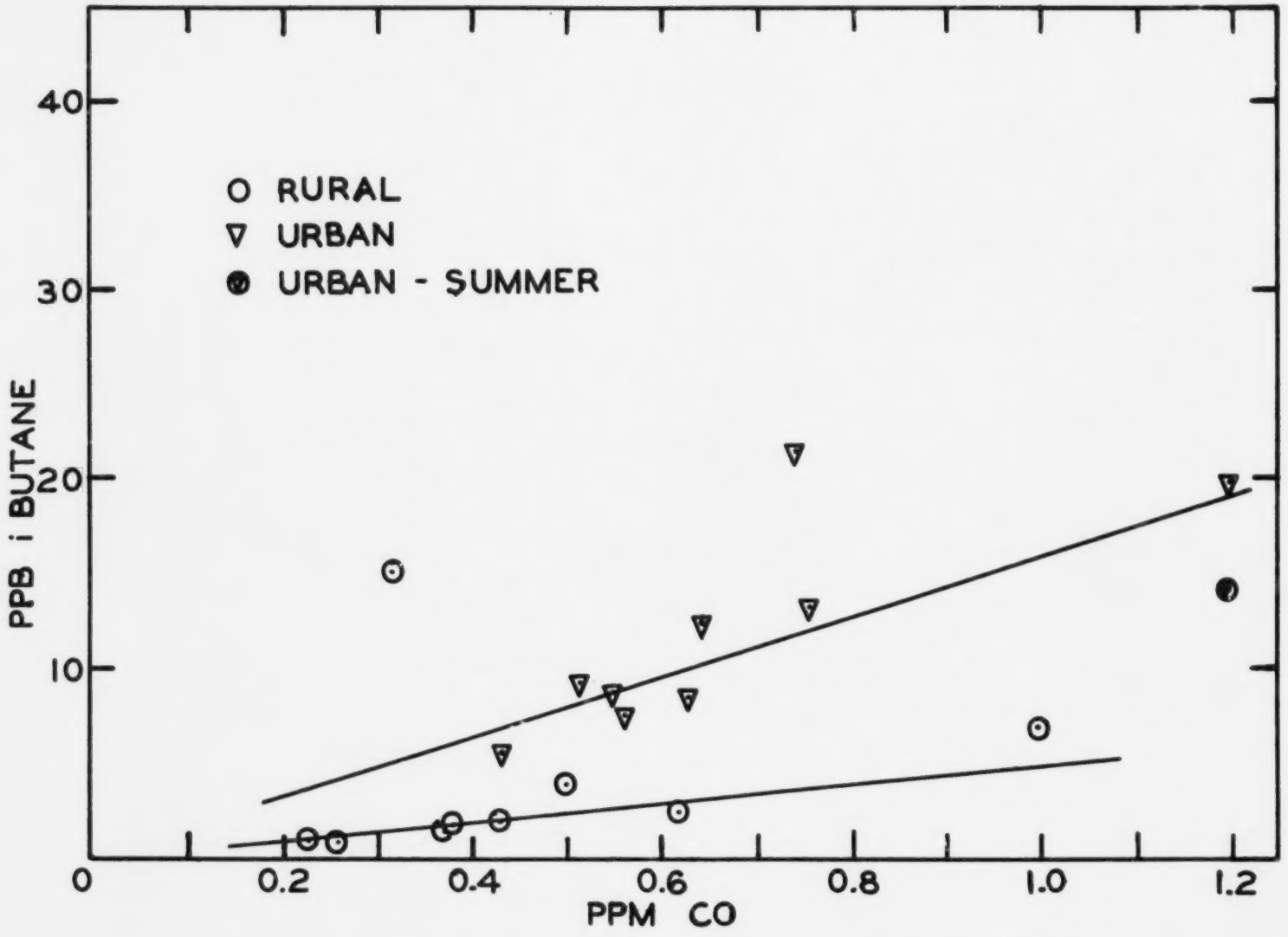

FIG. 12 PPB i-BUTANE VS. PPM CO IN ST. LOUIS, MISSOURI, AND VICINITY.

SECTION VII

REFERENCES

1. Stevens, C.M., Krout, L., Walling, D., Venters, A., Engelkemeir, A. and Ross, L. E., The Isotopic Composition of Atmospheric Carbon Monoxide. Earth and Planetary Science Letters, 16, 147-165 (1972).

2. Braham, R., University of Chicago, private communication.

3. Stevens, C.M. and Krout, L., Method for Determination of the Concentration and the Carbon and Oxygen Isotopic Composition of Atmospheric Carbon Monoxide. Int. J. Mass. Spect. and Ion Physics, 8, 265-275 (1972).

4. Kroopnick, P. and Craig, H., Atmospheric O_2: Isotopic Composition and Solubility Fractionation. Science, 175, 54 (1972).

5. Inman, R. E., Ingersoll, R. B. and Levy, E. V., Soil: A Natural Sink for Carbon Monoxide. Science, 172, 1229 (1971).

6. Weinstock, B., The Residence Time of Carbon Monoxide in the Atmosphere. Science, 166, 224 (1969).

7. Weinstock, B. and Niki, H., Carbon Monoxide Balance in Nature. Science, 176, 290 (1972).

8. Hurn, R. W., Air Pollution, Vol. III, p. 68 (1968), second edition, edited by A. C. Stern, Academic Press, New York.

9. Air Pollution, Vol. III, p. 662 (1968), A. C. Stern, Editor, Academic Press, New York.

10. O'Neil, J. R. and Epstein, S., A Method for Oxygen Isotope Analysis of Milligram Quantities of Water and Some of Its Applications. J. Geophys. Res., 71, 4955 (1966).

SECTION VIII

APPENDICES

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APPENDIX A. Conditions for Samples Collected in St. Louis, Missouri

Sample No.	Time	Temperature (°F)	Wind Speed (mph)	Wind Direction Degrees	Location
1. Conditions for Samples Collected June 27, 1973					
1 (1)*	0740	70	5	225 partly cloudy	At base of lookout tower, 5 miles, SSW of Otto, Mo., 29 miles, 220° from St. Louis. Hilltop location, valley to SW wooded area.
2 (2)	0920	80	5	270 clear	CAMP Station, 12th & Clark, St. Louis, traffic light.
3 (3)	1310	85	5	270 clear	New Memphis, Ill., 1 mile W of the New Memphis L&N station, 0.5 mile S of the tracks, along side a soybean field, level open country. Few patches of woods to W, farm buildings 1-2 miles to W, 31 miles, 113° from St. Louis.
4 (4)	1415	85	5	270 clear	New Minden, Ill., 47 miles, 108° from St. Louis, 1.5 miles N of New Minden on Ill. Rte. 127 in open field, soybean field to right, grass to left, woods to west, 0.5 mile N, 18 miles east of sample point 3.
4a	1430	85	5	270 clear	As above.
5 (5)	1510	15	5	270 clear	Carlyle, Ill., 47 miles, 86° from St. Louis, 6 miles N of Carlyle on Rte. 127, 0.5 mile W of Rte. 127 in open corn field. Corn 18" high, woods to W, East-West road 260 yds. N of sample point. 16 miles N of sample point 4.
2. Conditions for Samples Collected July 17, 1973					
1 (6)	0745	70	2	90 slightly overcast	18 miles, 171° from St. Louis 1 mile east of Ill. Rte. 3 on New Hanover Rd. at base of microwave tower, soybean field to east.
2 (2)	0850	72	2.5	112 slight overcast	CAMP Station 12th & Clark.
3 (7)	1340	88	2.5	90 slight overcast	25 miles, 270° from St. Louis on hill, 3-4 miles south of Missouri River where U.S. 40 crosses. The river plain to north rolling hills, woods and farms to east.
4 (8)	1433	85	5	90 clear	26 miles, 282° from St. Louis, 3 miles east of Weldon Springs on country road. Soybean field to east and southeast, rolling, partially wooded country side.

*Location on Map D-1.

APPENDIX A. (Con't.)

Sample No.	Time	Temperature (°F)	Wind Speed (mph)	Wind Direction Degrees		Location
			2. Conditions for Samples Collected July 17, 1973			
5 (9)*	1535	85	5	90	clear	33 miles, 277° from St. Louis, 1 mile east of intersection of county roads D & DD at former site of lookout tower. Open field to east & southeast bounded by woods.
5a (9)	1550	85	5	90	clear	
			3. Conditions for Samples Collected, November 13 and 14, 1973			
1 (10)	0630		10-12	180	clear	7.8 miles, 348° from St. Louis. ∿ 300 yards east of Bethlehem cemetery, on road to electric sub-station. Ravine and unused warehouse to south.
2 (10)	0730		12	160	clear	
3 (10)	0845		8-10	160p.	cloudy	
4 (10)	1022		8-10	210	cloudy	
5 (1)	1830		5-8	250	cloudy	29 miles, 220° from St. Louis. 5 miles SW Otto, Mo. at base of lookout tower.
6 (10)	0630		5	160	cloudy	as in one above
7 (10)	0730		5-8	160	cloudy	as in one above
8 (10)	0920		11	180	partly cloudy	as in one above
9 (11)	1030		12	180	clear	15.3 miles, 357° from St. Louis. 1.5 miles east of Rte. 67, ∿ 0.5 mile N Missouri River.
10 (10)	1120		16	180	clear	as in one above

* Location on Map D-1.

APPENDIX B. Conditions for Samples Collected along I-55 Argonne, Ill.

Sample No.	Time	Temperature (°F)	Wind Speed (mph)	Wind Direction Degrees	Location
			1. Samples Collected July 31, 1973		
1 (1)*	0940	72	8-10	30° cloudy	0.8 miles N I-55, 200 yds. W of Williams Rd. Soybean field to North.
2 (2)	1000	72	8-10	30° cloudy	30 ft. S of I-55, 0.1 mile E of Williams Rd. along Frontange Rd., traffic light to moderate.
3 (3)	1020	72	8-10	30° cloudy	0.5 mile S of I-55 on E side of Williams Rd. Soybean field to N, swamp grass to E. and N.
4 (4)	1040	74	8-10	30° cloudy	1.5 miles S of I-55 on E side of Weber Rd. (a continuation of Williams Rd.) ∿ 0.5 miles S of 135th street., cornfield to E and N, ∿ 6' high, intermittent traffic on road, shut down during and after traffic.
5 (5)	1117	74	8-10	30° cloudy	3.5 miles S of I-55 on Weber Rd., 0.3 miles S of Plainfield-Lockport Rd., soybean field to E and N.
			2. Samples Collected August 9, 1973		
1 (6)	1700	88	10-12	240-270° clear	3.3 miles W I-55, 0.8 miles S Ill. 126, 40 yds, W County Line Rd., corn field to N, cut oat field to S.
2 (7)	1733	85	10-12	240-270° clear	30 ft. E of I-55 0.2 miles S of Plainfield Rd., along Frontage Rd., Avg. 24 cars & 3 trucks/min.
2a	Duplicate of 202, pumped at same time				
3 (8)	1800	85	10-12	240-270° clear	0.5 miles E of I-55 100 yds. S of intersection of roads 0.5 mile E of I-55, 1 mile N of Plainfield Rd., level, open soybean field to I-55.
4 (9)	1823	85	10-12	240-270° clear	2 miles E of I-55, 30 yds. N of road, 1 mile N of Plainfield Rd., in cut oat field, soybean field to W.

* Locations on Map D-2.

APPENDIX C

Conditions for Samples Collected in Diurnal Studies
Plainfield, Illinois

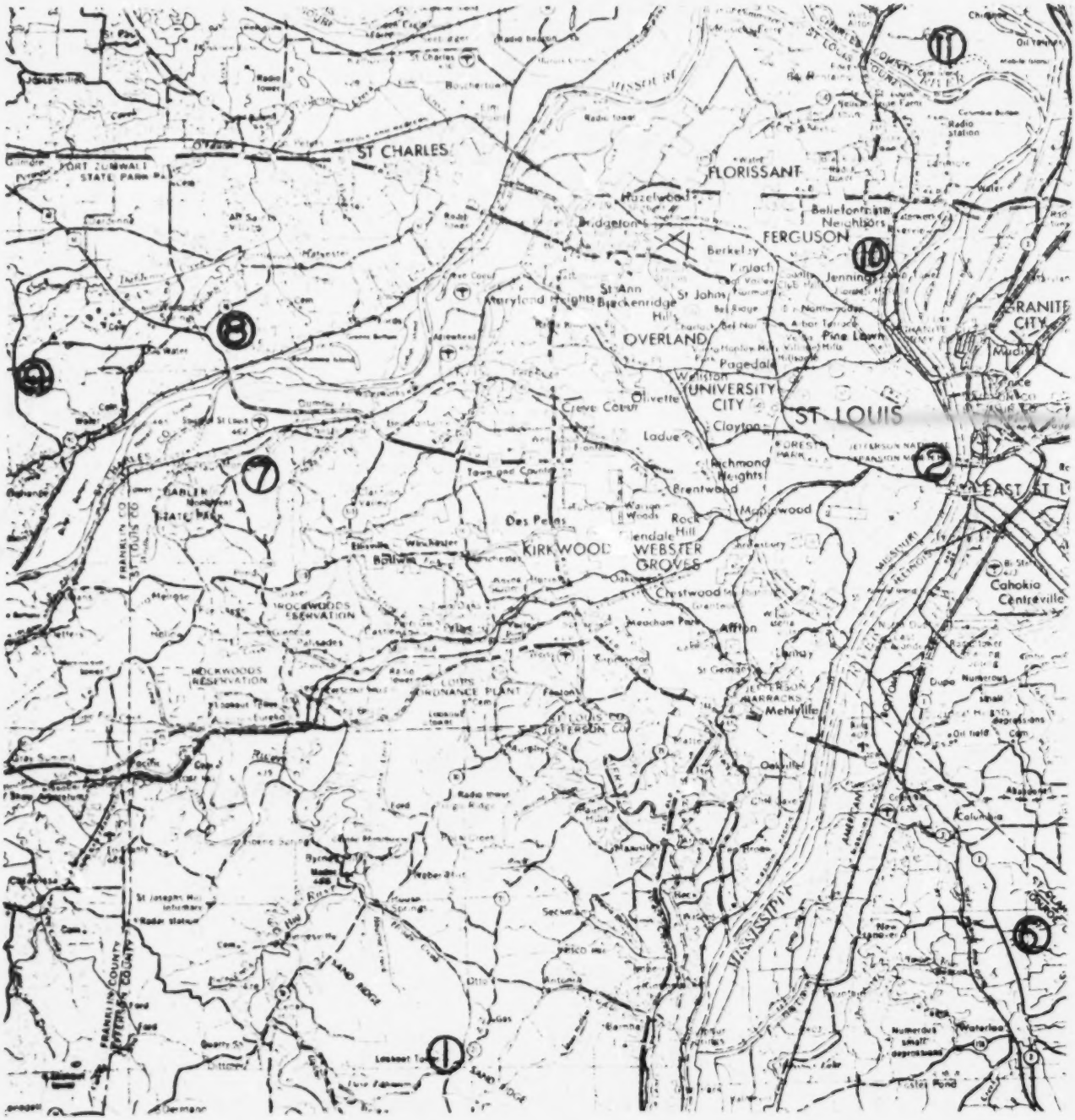
1. Samples Collected September 5, and 6, 1973:

Sample No.	Time	Temp.	Wind Speed	Wind Direction		Location
1	1655	79°F	5-8	290°		Cornfield, 3 miles West of Plainfield, Ill. 0.5 miles South of Ill. 126, 150 yards West - Ridge Road. Samples taken 3 feet above ground, 6 rows from South edge of corn-field. Corn was mature, but still green, 7 to 8 feet tall. Weather: Clear
2	2030	70°F	2-5	280°		
3	0030	56°F	2-5	300°		
4	0230	50°F	2-5	280°		
5	0500	46°F	2-5	290°		
6	0600	46°F	2-5	290°		
7	0730	56°F	2-5	300°		
8	1007	72°F	4-8	315°		
9	1655	75°F	3-5	290°		
2. Samples Collected June 11, 1974:						
1	0130	53°F	light & variable		ptly cloudy	Location as above but 15 yards West of Ridge Road, at edge of plowed field.
2	0315	48°F	calm		clear	
3	0445	54°F	1-2	315°	cloudy	
4	0635	56°F	1-2	225°	ptly cloudy	
5	1345	68°F	15-20	270°	cloudy	
3. Samples Collected July 18, 1974:						
1	0055	73°F	5-7	225°	ptly cloudy	Location as above, but 0.1 mile North at end of lane grass and alfalfa to South and West-ground sloped away to South and West.
2	0230	73°F	8-10	225°	cloudy	
3	0355	72°F	5-8	225°	cloudy	
4	0540	73°F	8-10	225°	cloudy	
5	0950	80°F	5-7	225°	cloudy	

* All samples location 10 Map D-2.

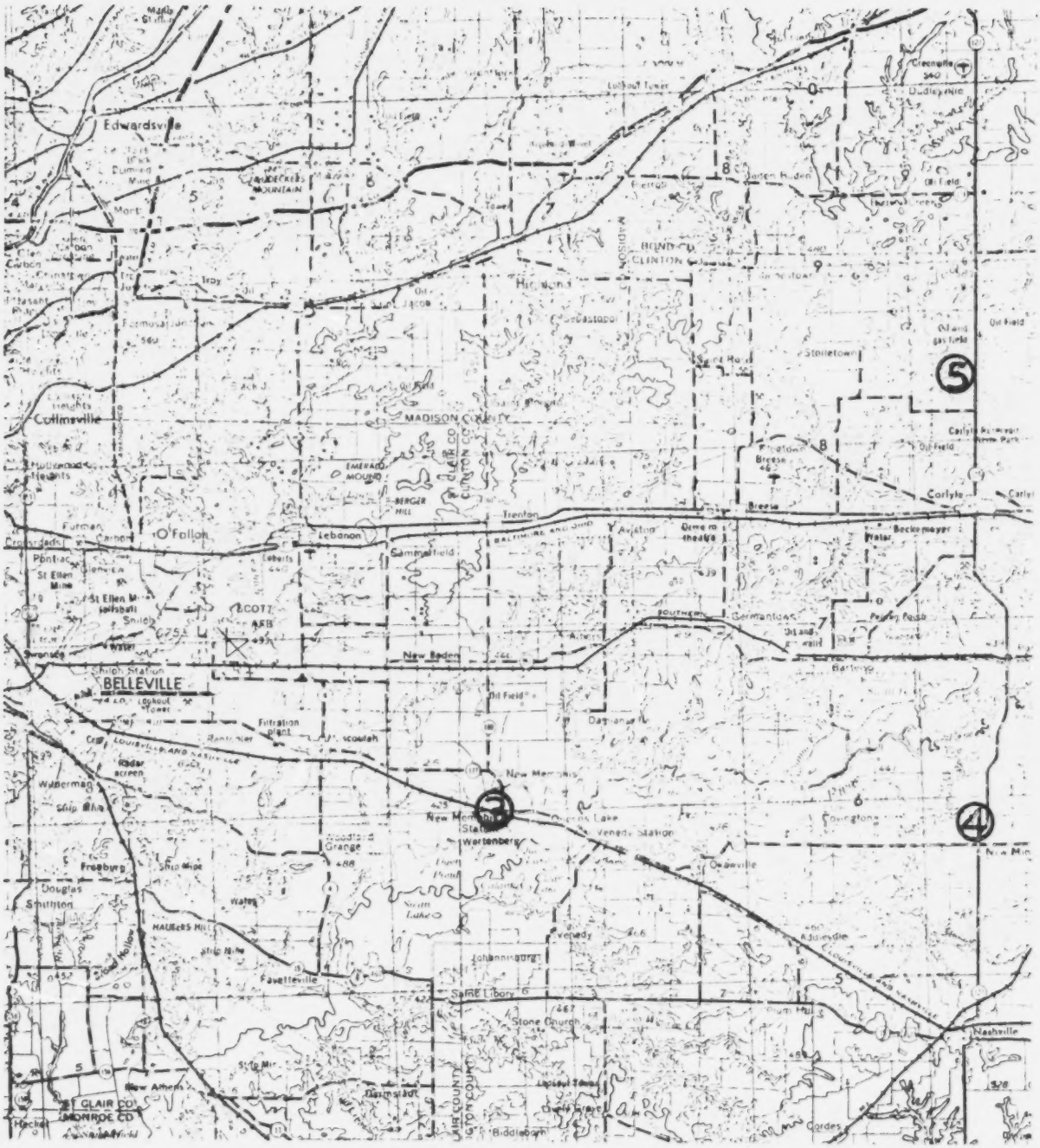
APPENDIX D. Maps of Sampling Locations

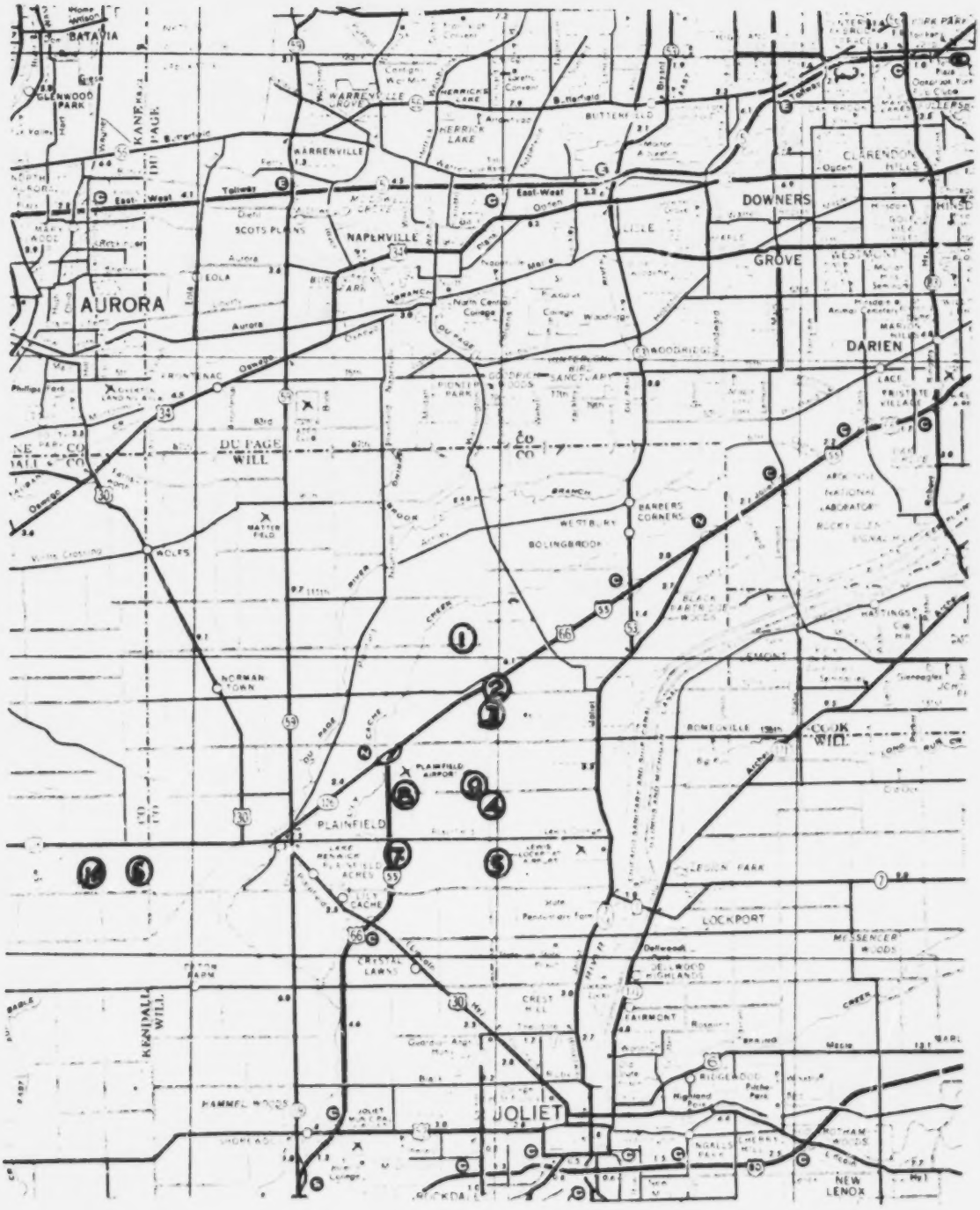
1. St. Louis, Missouri	June 27, 1973	Points 1-5
	July 17, 1973	Points 2, 6-9
	November 13, 14, 1973	Points 1, 10, 11
2. Plainfield, Illinois	July 31, 1973	Points 1-5
	August 9, 1973	Points 6-9
	September 5, 6, 1973	Point 10
	June 11, 1974	Point 10
	July 18, 1974	Point 10



APPENDIX D-1

Sampling Locations in St. Louis, Missouri


Edwardsville
Collinsville
MADISON COUNTY
CLAIR CO
CLINTON CO
O'Fallon
Lebanon
Trenton
Carlyle
BELLEVILLE
SCOTT AFB
New Baden
Shiloh Station
Filtration plant
Radar screen
Wabermag
Ship Rte
New Memphis
Wertenberg
Freeburg
Douglas
Shiloh
Grange
Venedy
Johannisburg
Fayetteville
Saint Libory
Stone Church
Nashville
New Athens
Darmstadt
Baldwin
CLAIR CO
MONROE CO
CLINTON COUNTY
WASHINGTON COUNTY
Germantown
Pocahontas
Beckemeyer
Aviston
Sandoval
Centralia
Carlyle
Breese
Trenton
Lebanon
Summerfield



APPENDIX D-2

Sampling Locations in Plainfield, Illinois, and along I-55